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(71) Applicant: ALLIED CORPORATION  
Columbia Road and Park Avenue P.O. Box 2245R (Law  
Dept.)  
Morristown New Jersey 07960(US)

(72) Inventor: DeAntonis, Ferdinand Anthony  
14 Trails End  
Fogelsville Pennsylvania 18051(US)

(72) Inventor: Murrell, William Henry  
104 Village Road  
R.D. 1, Orwigsburg Pennsylvania 17961(US)

(74) Representative: Baillie, Iain Cameron et al,  
c/o Langner Parry Isartorplatz 5  
D-8000 München 2(DE)

(54) Coextrusion of thermoplastic fluoropolymers with thermoplastic polymers.

(57) The present invention is a multilayered coextruded film and process of coextruding. The coextruded film comprises at least one thermoplastic fluoropolymer layer and at least one thermoplastic polymeric layer adjacent to the thermoplastic fluoropolymer layer. There is preferably a coextruded adhesive layer between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer. The coextruded film can be oriented in at least one direction and/or embossed without delamination, fibrillating, or splitting.

**EP 0 132 583 A2**

COEXTRUSION OF THERMOPLASTIC FLUOROPOLYMERS WITH  
THERMOPLASTIC POLYMERS

BACKGROUND OF THE INVENTION

The present invention is in the field of thermoplastic coextrusions; more particularly, the invention relates to coextrusions of thermoplastic fluoropolymers with thermoplastic polymers.

It is generally known how to coextrude film and sheet as indicated in the Modern Plastics Encyclopedia, Vol. 56, No. 10A, pp. 131-132, McGraw Hill, October, 1979. Coextruded sheet and film, are made using multimanifold dies such as a multimanifold circular die for blown film or a coextrusion feedblock for flat cast film and sheet. The article "Trends & equipment... Coextrusion" by M.H. Naitove in Plastics Technology, February, 1977, pp 61-71, discusses coextrusion in further detail. For the purposes of this invention the term film includes both film and sheet unless otherwise indicated.

A variety of different thermoplastics have been coextruded to form multilayered coextruded film to take advantage of different properties in different layers. Typical multilayered coextruded film include different thermoplastic polymeric layers having specific characteristics desired in coextruded film. Coextruded films could include a layer of polyethylene or polypropylene to provide a moisture barrier. The coextruded film can incorporate a layer of ionomer or nylon to improve toughness, or a layer of nylon as an oxygen barrier. A layer of polyvinylidene chloride can be included as an oxygen and moisture barrier. A layer of ethylene vinyl acetate copolymer or an ionomer can be included to provide heat sealability to a multilayer coextruded film.

Thermoplastic fluoropolymers can be extruded or solution cast to form films. These materials offer excellent chemical resistance and barrier properties. However, fluoropolymers have not been coextruded to form

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multilayered film structures. This could be due to difficulty in adhering fluoropolymer film layers to other thermoplastic layers.

#### SUMMARY OF THE INVENTION

5       The present invention is a multilayered coextruded film and process of coextruding. The coextruded film comprises at least one thermoplastic fluoropolymer layer and at least one thermoplastic polymeric layer adjacent to the thermoplastic fluoropolymer layer. There is preferably a coextruded adhesive layer between each  
10 thermoplastic fluoropolymer layer and each thermoplastic polymeric layer. The coextruded film can be oriented in at least one direction and/or embossed without delamination, fibrillating, or splitting.

15       The present invention also includes a process of coextruding a multilayered film. The process comprises the steps of coextruding at least one thermoplastic fluoropolymer layer adjacent to at least one thermoplastic polymeric layer. An adhesive layer is preferably coextruded between each thermoplastic fluoropolymer  
20 layer and each thermoplastic polymeric layer. The process can optionally include the steps of orienting and/or embossing the coextruded film.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

25       The present invention is a multilayered coextruded film and process to coextrude a multilayered film. Briefly, the coextruded film has at least one thermoplastic fluoropolymer layer and at least one thermoplastic polymeric layer adjacent to the thermoplastic fluoropolymer layer. There is preferably an adhesive  
30 between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer. The adhesive layer preferably comprises at least one modified polyolefin. The preferred modified polyolefins are modified ethylene vinyl acetate copolymers. The coextruded film can be  
35 oriented in at least one direction and/or embossed.

For the purposes of the present invention coextruded film includes sheets as well as films unless

otherwise indicated. The coextrusion is particularly useful as multilayered coextruded film as opposed to thicker sheets. Very thin fluoropolymer layers can be coextruded with thermoplastic polymeric layers to form the multilayered coextruded film of the present invention. A thin layer of the thermoplastic fluoropolymer is often all that is needed to take advantage of the excellent chemical resistance of thermoplastic fluoropolymers while at the same time minimizing the amount of thermoplastic fluoropolymer in the multilayered coextruded film. This is particularly advantageous considering the cost of thermoplastic fluoropolymers in comparison to the general variety of thermoplastic film forming polymeric materials available.

The thickness of each layer in the coextruded film is at least  $0.13 \times 10^{-2}$  mm (0.05 mils). Each layer can range from  $0.13 \times 10^{-2}$  (0.05 mils) to layers as thick as 6.35 mm (250 mils). Film can have layers which are preferably from  $0.254 \times 10^{-2}$  to 0.635 mm (0.1 to 25 mils) thick, while sheets can have thicker layers as well as thin layers. The preferred thickness range of the film is from  $0.254 \times 10^{-2}$  to 0.635 mm (0.1 mil to 25 mils), preferably  $1.27 \times 10^{-2}$  to 0.254 mm (0.5 to 10 mils). The thickness of the adhesive layer is greater than  $0.13 \times 10^{-2}$  mm (0.05 mils), and preferably ranges from  $0.13 \times 10^{-2}$  mm (0.05 to 0.5 mils), and more preferably  $0.254 \times 10^{-2}$  to 0.762 mm (0.1 to 0.3 mils). The multilayer films of the present invention are particularly useful where layer thicknesses are between  $0.13 \times 10^{-2}$  to  $1.27 \times 10^{-2}$  (0.05 to about 0.5) and preferably  $0.13 \times 10^{-2}$  to  $0.254 \times 10^{-2}$  mm (0.05 to 0.1 mils). Layers in this range cannot readily be made by other methods to form multilayered films.

The structure of the coextruded film of the present invention can vary. A thermoplastic fluoropolymer layer in the extruded film can vary from 1 to 99% of the thickness of the total structure. Alternately, the thermoplastic polymeric layer can vary from 1 to 99% of

the thickness of the total structure. There should be a sufficient amount of the adhesive to prevent delamination.

5 The multilayered coextruded film of the present invention can have a variety of structures so long as there is an adhesive layer between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer. A typical film structure includes a thermoplastic polymeric layer, an adhesive layer and a thermoplastic fluoropolymer layer. Another structure envisioned includes a layer of thermoplastic fluoropolymer, 10 an adhesive layer, a thermoplastic polymeric layer, an adhesive layer, and another thermoplastic fluoropolymer layer. Any variation of the order of the layers of the thermoplastic fluoropolymer and thermoplastic polymeric layer can be made. The number of layers in the multilayered coextruded film is only limited by the equipment. 15

The multilayer coextruded film of the present invention can be coextruded using coextrusion equipment generally known in the art. This includes coextrusion using a feed block with a standard die, a multimanifold circular die for blown bubble film, and multimanifold die for flat cast film and sheet. A coextrusion feed-block and flat die can be used for cast film. Useful 25 equipment is described in the article by Naitove referenced in the Background of the Invention and hereby incorporated by reference. The coextrusion process has advantages over other processes to form multilayered films. These advantages include the combination of molten layers in one step. Coextrusion allows a broad range of layer thickness variation, particularly at very thin ranges. 30

Thermoplastic fluoropolymers useful in the present invention are film-forming thermoplastic fluoropolymers. The thermoplastic fluoropolymers include, but are not limited to, ethylene chlorotrifluoroethylene copolymer, polychlorotrifluoroethylene, ethylene tetrafluoro- 35

ethylene copolymer, fluorinated ethylene-propylene copolymer (FEP), and polyvinylidene fluoride. Particularly preferred is ethylene chlorotrifluoroethylene copolymer.

5        Useful thermoplastic polymers include film-forming thermoplastic polymers. Such polymers include, but are not limited to, polyamides, polyolefins including polyethylene and polypropylene, polyolefin copolymers, ionomers such as neutralized olefin-carboxylic acid copolymers, polystyrene, polycarbonates, acrylic polymers, 10 copolymers, and fluoropolymers.

      Preferred polyamides include polyepsilon-caprolactam and polyhexamethylenedipamide. Other useful polyamides include film-forming polyamides made from the polymerization of lactam monomers, and the copolymerization of diamines and dicarboxylic acids. 15

      Polyolefins include low density polyethylenes, high density polyethylenes and polypropylenes. The polyolefin copolymers include the copolymers of ethylene and vinyl acetate, the copolymers of ethylene and vinyl 20 alcohol, the copolymers of ethylene and acrylic acid, the copolymers of ethylene and methylacrylate, and the copolymers of ethylene and ethylacrylate. Ionomers include the copolymers of polyolefins and alpha,beta-ethylenically unsaturated carboxylic acids neutralized 25 with metal salts. Ionomers include Surlyn® ionomers such as the copolymers of ethylene and methacrylic acid, with the carboxyl groups neutralized by metals including sodium and zinc.

30        The adhesive layer can be made of an extrudable adhesive which is compatible for coextrusion with the adjacent polymer layers. Preferably, the adhesive layer is made of a modified polyolefin copolymer such as ethylene vinyl acetate copolymer, or a blend of modified 35 polyolefins and another copolymer such as an olefin and ester copolymer. A modified polyolefin is one that has reactive groups, such as carboxylic acid groups incorporated into the polyolefin chain. Modified

polyolefins also can include carboxylic acid containing materials blended with the polyolefin. The most preferred modified polyolefin is the modified copolymer of ethylene and vinyl acetate. This copolymer is modified to contain carboxylic acid groups. This copolymer has been found to be particularly useful to form coextruded laminates of thermoplastic fluoropolymers and polyamides.

Preferred adhesives are CXA type resins sold by the Du Pont Company. These resins have been indicated to be useful for coextrusion of a variety of polymeric materials not including fluoropolymers. These resins have been found to be useful in the process of the present invention to make the multilayered coextruded film of the present invention. CXA 3101, CXA 1124, and CXA 1123 are particularly preferred. A detailed description of these CXA resins is found in the following bulletins hereby incorporated by reference: "Du Pont CXA, Coextrudable Adhesive Resins For Multilayer Packaging Structures" by Philip S. Blatz; "Du Pont CXA 3101, Coextrudable Adhesive Resin For Flexible Packaging"; and "Du Pont CXA 1123 & 1124". ELVAX® EVA 3135X Ethylene Vinyl Acetate Copolymer Resin For Flexible Packaging describes a resin useful to vary the viscosity of the resin selected for use as the adhesive layer. Resins such as CXA 3101 and CXA 1124 have been found to be satisfactory for coextrusion to form films having layers of fluoropolymers at temperatures above the recommended adhesive processing temperature limit of 230°C to 240°C (446°F to 464°F).

The adhesive layer can be a blend of at least two modified polyolefins. Preferred modified polyolefins are modified ethylene vinyl acetate copolymers, which are modified to have acid groups in addition to ester groups. A preferred blend comprises a first modified ethylene vinyl acetate copolymer having a melt index of about 0.1 to 10 grams per 10 minutes, and a second modified ethylene vinyl acetate copolymer having a melt



index of from 5 and preferably 10 to 200 grams per 10 minutes. For the purposes of the present invention, melt index is measured according to ASTM Test No. D-1238. The blend of the first and second polyolefin should comprise from 25 to 99%, preferably 50 to 95% and more preferably 75 to 95% of the first polyolefin based on the blend of the first polyolefin and the second polyolefin. Correspondingly there is 1 to 75%, preferably 5 to 50% and more preferably 5 to 25% of the second polyolefin.

The most preferred modified ethylene vinyl acetate copolymer for use as the first polymer is CXA-3101 produced by Du Pont and has a melt index of 3.5 (ASTM D-1238), a density of 0.948 grams per cubic centimeter (ASTM D-792), and the softening point of 131°F (ASTM D-1525). The most preferred second modified ethylene vinyl acetate copolymer in an adhesive blend is CXA-1124 produced by Du Pont and has a melt index of 25 grams per 10 minutes, a density of 0.950 grams per cubic centimeter (ASTM D-792), and a softening point of 101°F (ASTM D-1525). The most preferred adhesive composition is a blend of 90% by weight CXA-3101 and 10% by weight CXA-1124.

Other useful adhesives include modified and unmodified ethylene methylacrylate copolymer and adhesives disclosed in U.S. Patent Nos. 4,058,647 and 4,254,169 hereby incorporated by reference.

The multilayer coextruded film of the present invention includes a coextrusion of the fluoropolymer and an adhesive layer adjacent to at least one side of the fluoropolymer layer.

In order to successfully coextrude the multilayered film of the present invention, the thermoplastic fluoropolymer layer, the adhesive layer, and the thermoplastic layer must be made of polymeric materials which are compatible in the coextrusion process. Compatibility can be indicated by melt properties which are similar as to allow coextrusion. Melt properties of interest include

melting points, melt indexes, apparent viscosity and melt stability. Non-compatibility of polymers in the coextrusion can result in the inability to form the film where adjacent layers have good adhesion and uniform thickness across the film width. Non-compatible polymers can result in streaky, mottled film. Typically, non-compatible extrudable polymers designed to form a clear multilayer film result in a mottled, cloudy film or poor polymer distribution. The compatibility of the various polymers from the above lists for use in the film laminates of the present invention can be determined by considering the above indicators of compatibility. Once the polymers having the desired properties are selected, experimental trials can be conducted to determine the optimum combination of relative properties in adjacent layers.

The polymers to be coextruded must not only be compatible, but they must be compatible within a relatively close temperature range so that they can be coextruded through a common die. It has been found that a limitation with modified ethylene vinyl acetate copolymer adhesives is their temperature stability. The highest temperature at which the materials (such as CXA 3101) can be extruded is between about 232°C and 243°C (450°F and 470°F). Generally, for fluoropolymers such as ethylene chlorotrifluoroethylene, the lowest processing temperatures is higher than the adhesive temperature range. A preferred set of processing melt temperatures for ethylene chlorotrifluoroethylene copolymer is 260°C to 277°C (500°F to 530°F). Preferred processing melt temperature for polymers to be coextruded to the ethylene chlorotrifluoroethylene is 232°C to 271°C (450°F to 520°F). For polyepsilon-caprolactam the lowest preferred range is 243°C to 271°C (470°F to 520°F) and for ethylene vinyl alcohol copolymer the preferred range is 232°C to 243°C (450°F to 470°F). The melt temperature can be adjusted within the limits to vary the melt viscosity to improve coextrusion compatibility.

The coextruded multilayer film of the present invention can be oriented and/or embossed. The multilayer film can be oriented without delaminating or fibrillating. The embossing and or orientation of the film can be conducted by methods known in the art. A typical process and range of conditions for monoaxially orienting a fluoropolymer and polyamide film laminate are similar to those disclosed for polyamides in U.S. Patent No. 4,362,585, hereby incorporated by reference. Alternately, the film laminate of the present invention can be biaxially oriented using a blown tube apparatus, or a tenter frame apparatus.

The film can be monoaxially drawn or biaxially drawn as required and considering the draw limitation of the polymers in the various layers. Typically, film can be monoaxially drawn to a draw ratio of from 1.5:1 to 10:1 and preferably from 1.5:1 to 6:1. Typically, film can be biaxially drawn to a draw ratio of from 1.5:1 to 10:1 and preferably 1.5:1 to 6:1 in the machine direction and from 1.5:1 to 10:1 and preferably 1.5:1 to 6:1 in the transverse direction. Draw ratio is an indication of the increase in the dimension in the direction of draw.

The film laminate of the present invention can be embossed by means known in the art if it is nonoriented or oriented. Typically, embossing can be accomplished using film embossing rolls.

It has been found that the multilayered coextruded film of the present invention does not delaminate whether or not it is oriented and/or embossed. Further upon orientation the multilayer film does not fibrillate.

The fluoropolymer layers of the coextruded films of the present invention have chemical inertness and allow the film to be used as cable wrap, in drug packaging applications, and as carrier films in process such as in framing copper clad laminates of electronic uses.

Several examples are set forth below to illustrate

the nature of the invention and the manner of carrying it out. However, the invention should not be considered as being limited to the details thereof. All parts are by weight or otherwise indicated.

#### EXAMPLES 1

5 A thermoplastic layer of polyepsiloncaprolactam having specific gravity of 1.13 (ASTM D-792) and a melting point of 420°F (250°C) was cast coextruded with an equimolar ethylene chlorotrifluoroethylene copolymer (ECTFE) having a specific gravity of 1.68. The poly-  
10 epsiloncaprolactam is sold by Allied Corporation as Capron® 8207F nylon (nylon 6). The relative formic acid viscosity was 73 measured in 90 percent formic acid at a concentration of 9.2 percent by weight. The ethylene  
15 chlorotrifluoroethylene (ECTFE) copolymer is sold by Allied Corporation as HALAR® 500. The ECTFE copolymer had a density of 1.68 gm/ml, and a melt index of 15 g/10 minutes as measured according to ASTM 1238 run at 275°F under a piston load of 2160 grams, and about 49 to 51  
20 mol percent ethylene and a corresponding amount of chlorotrifluoroethylene monomer. The adhesive utilized was a blend of modified ethylene vinyl acetate copolymers. The blend comprised 10% of CXA-1124 and 90% of CXA-3101, both sold by the Du Pont Co.

25 The polyepsiloncaprolactam was extruded through a 6.35 cm (2-1/2 inch) diameter Davis Standard Extruder having the temperature profile of Zone 1-210°C (410°F), Zone 2-232°C (450°F), Zone 3-271°C (520°F), Zone 4-254°C (490°F), Zone 5-254°C (490°F), and adaptor Zone 1-254°C (490°F). The extruder was operated at a screw speed of  
30 35 RPM with a barrel pressure of 6,895 kPa (1000 psig). The motor drive load was 36 amps. The melt temperature was (505°F).

35 The ethylene chlorotrifluoroethylene copolymer was extruded through a 4.45 cm (1-3/4 inch) (nominal) diameter Reifenhauer extruder. The extruder had a temperature profile which included Zone 1-232°C (450°F), Zone 2-271°C (520°F), Zone 3-282°C (540°F), Zone 4-274°C

(525°F), and the adaptor Zone at 254°C (490°F). This extruder was operated at a screw speed of 29 RPM with a barrel pressure of 4,482 kPa (650 psig). The motor drive load was 8.5 amps. The melt temperature was 272°C (522°F).

5 The adhesive blend was extruded through a 3.81 cm (1-1/2 inch) diameter Davis Standard Extruder. The temperature profile in this extruder was Zone 1-138°C (280°F), Zone 2-232°C (450°F), and adaptor Zone 1 at 10 228°C (443°F). This extruder had a screw speed of 20 RPM, a barrel pressure of 4,482 kPa (650 psig). The melt temperature was 224°C (435°F). The motor drive load was 2.5 amps.

15 The extrudate from the three extruders was passed through a coextrusion feedblock manufactured by the Johnson Plastic Corporation and operating at an adaptor temperature at Zone 1-248°C (478°F) and Zone 2-249°C (481°F). The laminate from the coextrusion adaptor went to a die having three Zones operating at about 263°C (505°F).

20 The coextruded film was then cast on a roll at 82°C (180°F), followed by a cooling roll at 63°C (145°F), and a roll at 79°C (175°F).

25 The film made had a total thickness of  $5.84 \times 10^{-2}$  mm (2.30 mils) with the following layers:  $0.99 \times 10^{-2}$  (1.36 mils) of polyepsilon-caprolactam (nylon 6), 0.39 mils of adhesive blend,  $3.9 \times 10^{-2}$  mm (1.55 mils) of ethylene chlorotrifluoroethylene copolymer (ECTFE). The adhesion between the layers of ECTFE copolymer and 30 nylon was tested according to ASTM Test No. ASTM F88. The adhesion and value was 305g/cm (775 g/in). The multilayer film was clear, had a uniform appearance, and uniform polymer distribution in each layer.

#### EXAMPLE 2

35 A five layer laminate was coextruded using the ECTFE copolymers and nylon 6 of Example 1. The adhesive utilized was a modified ethylene vinyl acetate copolymer, CXA-3101.

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The polyepsilon-caprolactam was extruded through the Davis Standard Extruder having the temperature profile of Zone 1-210°C (410°F), Zone 2-232°C (450°F), Zone 3-260°C (500°F), Zone 4-254°C (490°F), Zone 5-254°C (490°F), and adaptor Zone 1-254°C (490°F). The extruder was operated at a screw speed of 16 RPM with a barrel pressure of 6,895 kPa (1000 psig) and a motor drive load amperage of 45 amps. The melt temperature was 237°C (458°F).

The ethylene chlorotrifluoroethylene copolymer was extruded through a 4.445 cm (1-3/4 inch) (nominal) diameter Reifenhauer extruder. The extruder had a temperature profile which included Zone 1-232°C (450°F), Zone 2-277°C (530°F), Zone 3-285°C (545°F), Zone 4-288°C (550°F), and the adaptor Zone at 500°F. This extruder was operated at a screw speed of 40 RPM with a barrel pressure of 4,619 kPa (670 psig) and a motor drive load amperage of 115 amps. The melt temperature was 504°F.

The adhesive was extruded through a 3.81 cm (1-1/2 inch) diameter Davis Standard Extruder. The temperature profile in this extruder was Zone 1-121°C (250°F), Zone 2-246°C (475°F), and adaptor Zone 1 at 238°C (460°F). This extruder had a screw speed of 62 RPM and a motor drive load of 2.8 amps. The melt temperature was 202°C (396°F).

The extrudate from the three extruders was passed through a coextrusion feedblock manufactured by the Johnson Plastic Corporation and operating at an adaptor temperature at Zone 1-249°C (480°F) and Zone 2-249°C (481°F). The laminate from the coextrusion adaptor went to a die having three Zones operating at Zone 1-265°C (509°F), Zone 2-263°C (506°F), and Zone 3-263°C (506°F).

The coextruded film was then cast on a roll at 79°C (175°F), followed by a cooling roll at 88°C (190°F), and a roll at 110°C (230°F).

The film had a total thickness of  $2.54 \times 10^{-2}$  mm  $2.54 \times 10^{-2}$  mm (1.0 mils) with the following layers:  
 $0.254 \times 10^{-2}$  mm (0.1 mil) ECTFE copolymer/0.203 x

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10<sup>-2</sup> (0.08 mil) CXA 3101/1.63 x 10<sup>-2</sup> mm (0.64 mil) nylon  
6/0.203 x 10<sup>-2</sup> (0.08 mil) CXA 3101/0.254 x 10<sup>-2</sup> (0.1  
mil) ECTFE copolymer. The adhesion between the layers  
and ECTFE copolymer and nylon was tested as in Example  
1. The ECTFE layer, which was only 0.254 x 10<sup>-2</sup> mm (0.1  
mils), broke before delamination occurred. The  
multilayer film was clear, had a uniform appearance, and  
a uniform polymer distribution in each layer.

EXAMPLE 3

10 A five layer film was coextruded having layers of  
ethylene vinyl alcohol copolymer and ECTFE copolymer of  
the type described in Example 1. The adhesive was the  
same type as described in Example 2.

15 A thermoplastic layer of ethylene vinyl alcohol  
copolymer produced by Kuraray of Japan (Grade EP-f) was  
cast coextruded with layers of equimolar ethylene  
chlorotrifluoroethylene copolymer. The ethylene vinyl  
alcohol copolymer had a melt index of 1.6 grams per 10  
minutes as measured on the ASTM D-1238 test at a load of  
2160 grams at 190°C. The ethylene vinyl alcohol resin  
20 contained about 60 mole percent vinyl alcohol and had a  
glass transition temperature of 69°C.

The ethylene vinyl alcohol was extruded through a  
6.35 (2-1/2 inch) diameter Davis Standard Extruder  
25 having the temperature profile of Zone 1-143°C (290°F),  
Zone 2-193°C (380°F), Zone 3-227°C (440°F), Zone 4-227°C  
(440°F), Zone 5-210°C (410°F), and adaptor Zone 1-246°C  
(475°F). The extruder was operated at a screw speed of  
19 RPM with a barrel pressure of 3,447 kPa 500 psig and  
30 a motor drive load of 38 amps. The melt temperature was  
(407°F).

The ethylene chlorotrifluoroethylene copolymer was  
extruded through a 4.445 cm (1-3/4 inch) (nominal)  
diameter Reifenhauer extruder. The extruder had a  
35 temperature profile which included Zone 1-232°C (450°F),  
Zone 2-277°C (530°F), Zone 3-285°C (545°F), Zone 4-288°C  
(550°F), and the adaptor Zone at 260°C (500°F). The  
motor drive load was 11 amps. This extruder was

operated at a screw speed of 42 RPM with a barrel pressure of 4,826 kPa (700 psig). The melt temperature was 266°C (510°F).

The adhesive was extruded through a 3.81 cm (1-1/2 inch) diameter Davis Standard Extruder. The temperature profile in this extruder was Zone 1-121°C (250°F), Zone 2-246°C (475°F), and adaptor Zone 1 at 238°C (460°F). This extruder had a screw speed of 20 RPM, and a motor drive amperage of 2.6 amps. The melt temperature was 224°C (435°F).

The extrudate from the three extruders was passed through a coextrusion feedblock coextruder adaptor manufactured by the Johnson Plastic Corporation and operating at an adaptor temperature at Zone 1-249°C (480°F) and Zone 2-249°C (481°F). The laminate from the coextrusion adaptor went to a die having three Zones operating at Zone 1-265°C (509°F), Zone 2-263°C (506°F), Zone 3-263°C (506°F).

The coextruded film was then cast on a roll at 79°C (175°F), followed by a cooling roll at 85°C (185°F), and a roll at 110°C (230°F).

The film had a total thickness of  $2.54 \times 10^{-2}$  (1.0 mils) with the following layers:  $0.254 \times 10^{-2}$  mm (0.1 mil) ECTFE copolymer/ $0.203 \times 10^{-2}$  mm (0.08 mil) CXA 3101/ $1.63 \times 10^{-2}$  mm (0.64 mil) ethylene vinyl alcohol copolymer/ $0.203 \times 10^{-2}$  mm (0.08 mil) CXA 3101/ $0.254 \times 10^{-2}$  mm (0.1 mil) ECTFE copolymer. The adhesion between the layers of ECTFE copolymer and ethylene vinyl alcohol copolymer was tested as in Example 1. The ECTFE layer, which was only  $0.254 \times 10^{-2}$  mm (0.1 mil) thick broke before delamination occurred. The multilayer film was clear, had a uniform appearance, and a uniform polymer distribution in each layer.

#### EXAMPLE 4

A thermoplastic oriented coextruded multilayered film of polyepsilonecaprolactam and an equimolar ethylene chlorotrifluoroethylene copolymer of the type used in Example 1 was made. The adhesive utilized was a CXA



3101 modified ethylene vinyl acetate copolymer as described above.

5 The polyepsilon-caprolactam was extruded through a 6.35 cm (2-1/2 inch) diameter Davis Standard Extruder having the temperature profile of Zone 1-210°C (410°F), Zone 2-232°C (450°F), Zone 3-271°C (520°F), Zone 4-260°C (500°F), Zone 5-254°C (490°F), and adaptor Zone 1-258°C (496°F). The extruder was operated at a screw speed of 30 RPM with a barrel pressure of 7,584 kPa (1100 psig) and a motor drive amperage of 41 amps. The melt temperature was 252°C (486°F).

10 The ethylene chlorotrifluoroethylene copolymer was extruded through a 4.445 cm (1-3/4 inch) (nominal) diameter Reifenhauer extruder. The extruder had a temperature profile which included Zone 1-227°C (440°F), Zone 2-252°C (485°F), Zone 3-279°C (535°F), Zone 4-274°C (525°F), and the adaptor Zone at 260°C (500°F). This extruder was operated at a screw speed of 33 RPM; the motor drive amperage was 10 amps. The melt temperature was 270°C (518°F).

20 The adhesive was extruded through a 3.81 cm (1-1/2 inch) diameter Davis Standard Extruder. The temperature profile in this extruder was Zone 1-138°C (280°F), Zone 2-232°C (450°F), and adaptor Zone 1 at 225°C (437°F). This extruder had a screw speed of 33 RPM, The motor drive load was 2.6 amps. The melt temperature was 221°C (429°F).

25 The extrudate from the three extruders was passed through a coextrusion feedblock manufactured by the Johnson Plastic Corporation which was operated at an adaptor temperature at Zone 1-252°C (485°F) and Zone 2-252°C (485°F). The laminate from the coextrusion feedblock went to a die having three Zones operating at Zone 1-264°C (508°F), Zone 2-264°C (507°F) and Zone 3-262°C (503°F).

30 The coextruded film was then cast on a roll at 82°C (180°F), followed by a cooling roll at 63°C (145°F), and a roll of 77°C (170°F).

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5 The film was oriented monoaxially. It traveled over a preheated roll at 116°C (240°F), to a slow stretch roll at 113°C (235°F), to a fast stretch roll at 103°C (235°F), to a heat set roll at 121°C (250°F), and finally to a cooling roll at 93°C (200°F). The draw ratio was 3.2:1. A detailed description of the orientation process is discussed in U.S. Patent No. 4,362,585.

10 The final structure of the film laminate was  $0.56 \times 10^{-2}$  mm (0.22 mils) ECTFE copolymer/ $0.30 \times 10^{-2}$  mm (0.12 mil) CXA 3101 copolymer/ $1.68 \times 10^{-2}$  mm (0.66 mils) nylon 6. The adhesion between the layers of ECTFE copolymer and nylon was tested as in Example 1 after orientation. The adhesion value was  $2.56 \times 10^{-2}$  g/cm (650 g/in). The oriented multilayer film was clear, had  
15 a uniform appearance and uniform polymer distribution in each layer.

20 While exemplary embodiments of the invention have been described, the true scope of the invention is to be determined from the following claims.

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What is claimed is:

1. A coextruded film comprising at least one thermoplastic fluoropolymer layer, and at least one thermoplastic polymeric layer adjacent to the thermoplastic fluoropolymer layer.

2. The film as recited in claim 1 further comprising an adhesive layer between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer.

3. The film as recited in claim 1 wherein the thermoplastic fluoropolymer is selected from the class consisting of ethylene chlorotrifluoroethylene copolymer, polyvinylidene fluoride, ethylene tetrafluoroethylene copolymer, fluorinated ethylene-propylene copolymer, polychlorotrifluoroethylene and vinylidene fluoride and tetrafluoroethylene copolymer.

4. The film as recited in claim 1 wherein the thermoplastic polymeric layer is made from a thermoplastic selected from the class consisting of polyamide, polyethylene, polypropylene, polyolefin copolymers, ionomers, polystyrenes, polycarbonates, acrylic polymers and copolymers, and fluoropolymers.

5. The film as recited in claim 1 wherein the adhesive layer comprises a blend of a first modified ethylene vinyl acetate copolymer having a melt index of from about 0.1 to 10 g/10 minutes and the second modified ethylene vinyl acetate copolymer having a melt index from 5 to 1000 g/10 minutes, the second modified ethylene vinyl acetate.

6. The film as recited in claim 1 wherein the film is oriented in at least one direction.

7. The film as recited in claim 6 wherein the film is embossed.

8. A process of coextruding a multilayer film comprising the step of coextruding at least one thermoplastic fluoropolymer layer adjacent to at least one thermoplastic polymeric layer.

9. The process as recited in claim 8 further comprising the step of coextruding an adhesive layer

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between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer.

10. The process as recited in claim 8 further comprising the step of embossing the film.

5 11. The process as recited in claim 10 further comprising the step of orienting the film in at least one direction.

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(71) Applicant: **ALLIED CORPORATION**  
Columbia Road and Park Avenue P.O. Box 2245R (Law  
Dept.)  
Morristown New Jersey 07960(US)

(72) Inventor: **DeAntonis, Ferdinand Anthony**  
14 Trails End  
Fogelsville Pennsylvania 18051(US)

(72) Inventor: **Murrell, William Henry**  
104 Village Road  
R.D. 1, Orwigsburg Pennsylvania 17961(US)

(74) Representative: **Baillie, Iain Cameron et al,**  
c/o Langner Parry Isartorplatz 5  
D-8000 München 2(DE)

(54) **Coextrusion of thermoplastic fluoropolymers with thermoplastic polymers.**

(57) The present invention is a multilayered coextruded film and process of coextruding. The coextruding film comprises at least one thermoplastic fluoropolymer layer and at least one thermoplastic polymeric layer adjacent to the thermoplastic fluoropolymer layer. There is preferably a coextruded adhesive layer between each thermoplastic fluoropolymer layer and each thermoplastic polymeric layer. The coextruded film can be oriented in at least one direction and or embossed without delamination, fibrillating, or splitting.

**EP 0 132 583 A3**



European Patent  
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# EUROPEAN SEARCH REPORT

0132583  
Application number

EP 84 10 6982

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-3 549 389 (N. PETERSON)  * Claim 1; column 3, line 19 - column 4, line 48; column 6, line 1 - column 7, line 36; column 10, lines 15-19 *	1-4, 6, 8, 9	B 32 B 27/08 C 09 J 3/14 C 08 L 23/08
X	FR-A-2 436 676 (UGINE KUHLMANN)  * Claims 2,3; page 6, lines 3-35 *	1-4, 8, 9	
A	EP-A-O 079 178 (RAYCHEM) * Claims 1,3,9-11; page 4, lines 14-27; page 5, line 20 - page 7, line 14 *	5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 32 B C 09 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-10-1985	Examiner BLASBAND I.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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EPA/EPO/OEB  
D-80298 München  
+ 49 89 2399-0  
TX 523 656 epmu d  
FAX + 49 89 2399-4465

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Vereenigde,  
Nieuwe Parklaan 97  
2587 BN Den Haag  
PAYS-BAS

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Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire MITSUBISHI PLASTICS INC.	

**NOTIFICATION OF EUROPEAN PUBLICATION NUMBER AND INFORMATION ON THE APPLICATION OF ARTICLE 67(3) EPC**

The Receiving Section hereby informs you that the technical preparations for publication of the above-mentioned European patent application have been completed.

The provisional protection under Art. 67(1) and (2) EPC in the individual Contracting States becomes effective only when the conditions referred to in Art. 67(3) EPC have been fulfilled (for further information, see EPO brochure "National Law relating to the EPC").

This application will be published on 02.01.04 with the European search report. The publication will be mentioned in European Patent Bulletin number 2004/01

The publication number is: 1375134

The title of the invention in the three official languages of the European Patent Office is worded as follows:

Trennbare Mehrschichtfolie

Releasing laminated film

Film lamine a liberation

In all future communications to the EPO, please quote the application number as indicated above, i.e. including the final four figures (which identify the Directorate responsible for the subsequent procedure).

Amendments to a European patent application or European patent must be filed in the language of the proceedings.

REMARK: An issue of the published European patent application will be forwarded to you directly from our printer.

RECEIVING SECTION



### New Set of Claims

1. A releasing laminated film comprising a supporting film having a tensile modulus of elasticity in a traverse direction measured according to ASTM D882 of 980 to 6,860 N/mm<sup>2</sup> and a film comprising a fluororesin laminated on one side of the supporting film, the other side of the supporting film having a 10-point averaged surface roughness (Rz) of 3.0 to 8.0 µm and the number of peaks (Pc) of 200 to 400, both measured according to JIS BO 601.
2. The releasing laminated film according to claim 1, wherein Rz is 4.0 to 7.0 µm and Pc is 250 to 350.
3. The releasing laminated film according to claim 1 or 3, wherein said tensile modulus of elasticity in a traverse direction is in a range of from 2,940 to 5,880 N/mm<sup>2</sup>.
4. The releasing laminated film according to any one of claims 1 to 3, wherein the fluororesin is tetrafluoroethylene-ethylene copolymer resin and the film comprising the fluororesin has a thickness of 1 to 50 µm.
5. The releasing laminated film according to any one of claims 1 to 4, wherein the supporting film has a melting point of 110°C or higher.
6. The releasing laminated film according to any one of claims 1 to 5, wherein the supporting film is a polyester film having a thickness of 5 to 1,000 µm.
7. The releasing laminated film according to any one of claims 1 to 6, wherein the film comprising a fluororesin is dry laminated on the supporting film.
8. The releasing laminated film according to any one of claims 1 to 7, wherein a polyethylene film, polypropylene film, or polyester film is further laminated on the film comprising a fluororesin.



New page 2

9. The releasing laminated film according to any one of claims 1 to 8, wherein the film has a total thickness of 10 to 300  $\mu\text{m}$ .
10. The releasing laminated film according to any one of claims 1 to 9, wherein th film has a total thickness of 60 to 300  $\mu\text{m}$ .